

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

REC'D 30 AUG 2004



Applicant's or agent's file reference BPX 9702		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)
International application No. PCT/GB 03/03428	International filing date (day/month/year) 06.08.2003	Priority date (day/month/year) 15.08.2002
International Patent Classification (IPC) or both national classification and IPC E21B43/25		
Applicant BP EXPLORATION OPERATING COMPANY LIMITED et al.		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 5 sheets.

- This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 26.02.2004	Date of completion of this report 27.08.2004
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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/GB 03/03428**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-20 as originally filed

Claims, Numbers

1-38 filed with telefax on 16.06.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB 03/03428

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-38
	No: Claims	
Inventive step (IS)	Yes: Claims	1-38
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-38
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Amendments :

- 1.1** The amendments filed with the letter dated 16.06.2004 are allowable considering Article 19(2) PCT.

2. Novelty :

- 2.1** Since none of the documents cited in the search report disclose all the features of independent **claims 1 or 2**, it is considered that said claims, as well as dependent **claims 3-23**, are novel over said prior art documents. In particular, none of the prior art documents disclose a method where the gelling composition enters the pores of the formation to form a gel, thereby encapsulating the production chemical.
- 2.2** Since none of the documents cited in the search report disclose all the features of independent **claim 24**, it is considered that said claim, as well as dependent **claims 25-37 and claim 38**, are novel over said prior art documents.

3. Inventive step :

- 3.1 Document D1** discloses a method for releasing substances into downhole environments. Said method comprises the steps of
- encapsulating a production chemical in an appropriate matrix, such as resin, starch or other polysaccharides material, e.g. gellable polymer (see p11 l20-31).
 - inserting the obtained solid particles into the well (into fissures, fractures, etc..) (see p13 l15-24)
 - delayed and controlled release of the production chemical.

Said production chemical can be a scale inhibitor, a corrosion inhibitor, an asphaltene control chemical, gel breakers, etc (see p12 l1-13).

Document D2 (see col2 - col4), disclosing the injection into a subterranean formation of a gelling composition comprising a carboxylate-containing polymer, a crosslinking agent and an aqueous liquid (brine).

- 3.2** The method of **claims 1 or 2** the present application differs from the method disclosed in **document D1**, considered as being the closest prior art document, in that the gelling composition enters the pores of the formation where the polymer forms a gel, thereby encapsulating the production chemical in the gel.

Since none of the prior art document teaches or fairly suggests a method where the gelling composition enters the pores of the formation to form a gel, thereby encapsulating the production chemical it appears to be non-obvious to the skilled person.

Hence, **claims 1 and 2**, as well as dependent **claims 3-23**, are considered as being inventive.

- 3.3** The subject-matter of claim 24 differs from the disclosure of the prior art documents in that :

- in **D1**, the oil production chemical is encapsulated in solid particles. Furthermore, there is no indication about the gellation rate.
- in **D2**, a gelling composition is disclosed, but there is no suggestion that a production chemical may be incorporated into said composition. Said **document D2** teaches that the gelation rate is usually longer than about 1 hour in this kind of composition (see col3 l28-40).

However, nothing in D2 or in the other prior art documents, would incite the skilled person to incorporated in a composition as disclosed in D2, an oil production chemical as defined in the present application.

Therefore, claims 24-38 are considered as being inventive.

Case No: 9702(2)

Claims

1. A method of introducing an oil field or gas field production chemical into a hydrocarbon-bearing porous subterranean formation penetrated by a wellbore comprising:
injecting a gelling composition comprising an aqueous liquid, an oil field or gas field
5 production chemical, and a gellable polymer through the wellbore into the porous subterranean formation wherein the gellable polymer forms a gel within the pores of the subterranean formation thereby encapsulating the production chemical in the gel; and controllably releasing the production chemical from the gel into a formation fluid.
2. A method of increasing the effectiveness of an oil or gas field production
10 chemical by reducing the number of squeezing and shut-in operations needed to increase the production rate from a wellbore penetrating a hydrocarbon-bearing porous subterranean formation, said method comprising:
 - A) injecting a gelling composition comprising an aqueous liquid, an oil or gas field
15 production chemical and a gellable polymer through the wellbore into the porous subterranean formation wherein the polymer forms a gel in the formation thereby encapsulating the oil or gas field production chemical in the gel;
 - B) after injecting the gelling composition, optionally over-flushing the porous
subterranean formation with an aqueous fluid or an oil;
 - C) subsequently, shutting-in the well for a period of time; and
 - 20 D) putting the well back on production and controllably releasing the oil or gas field production chemical from the gel into a formation fluid that is being produced from the well.
3. A method as claimed in Claims 1 or 2 wherein the gelling composition

comprises (i) an aqueous liquid, (ii) an oil or gas field production chemical, (iii) a gellable polymer having crosslinkable groups, and (iv) a crosslinking agent and wherein the gel is formed within the pores of formation through crosslinking of the crosslinkable groups of the gellable polymer with the crosslinking agent.

5 4. A method as claimed in any one of the preceding claims wherein the production chemical is controllably released from the gel into the formation fluid in the near wellbore region of the formation.

5. A method as claimed in any one of the preceding claims wherein the formation fluid is selected from the group consisting of a formation brine, crude oil, natural gas and
10 gas field condensate.

6. A method as claimed in any one of Claims 3 to 5 wherein the gellable polymer is dispersed or dissolved in a first aqueous fluid (hereinafter "polymer slug"), the crosslinking agent is dissolved in a second aqueous fluid (hereinafter "crosslinking agent slug"), the production chemical is dispersed, suspended or dissolved in the polymer slug
15 and/or the crosslinking agent slug and the gelling composition is formed within the pores of the formation by either: (a) injecting the polymer slug into the porous subterranean formation prior to injecting the crosslinking agent slug and back-producing the polymer slug over the crosslinking agent slug or (b) injecting the crosslinking agent slug into the porous subterranean formation prior to injecting the polymer slug and back-producing
20 the crosslinking agent slug over the polymer slug.

7. A method as claimed in Claim 6 wherein an aqueous spacer is injected between the polymer slug and crosslinking agent slug and optionally an aqueous pre-flush fluid is injected into the porous subterranean formation prior to injection of the polymer slug, crosslinking slug and aqueous spacer.

25 8. A method as claimed in Claim 7 wherein the production chemical is dissolved, dispersed or suspended in one or more of the aqueous pre-flush fluid, the polymer slug, the crosslinking agent slug or aqueous spacer.

9. A method as claimed in any one of the preceding claims wherein the oil or gas field production chemical is selected from the group consisting of (i) scale inhibitors,
30 (ii) corrosion inhibitors, (iii) hydrogen sulphide scavengers and (iv) hydrate inhibitors.

10. A method as claimed in any one of the preceding claims the production chemical is suspended in the aqueous liquid in the form of particles having a particle size of 100% less than 10 microns.

11. A method as claimed in Claim 10 wherein the particles of production chemical are coated with a coating agent selected from water-soluble polymers and oil-soluble polymers.
12. A method as claimed in any one of the preceding claims wherein the gellable polymer is selected from the group consisting of biopolysaccharides, cellulose ethers and acrylamide-containing polymers.
13. A method as claimed in any one of the preceding claims wherein the concentration of the gellable polymer in the gelling composition is in the range of about 0.01 to 0.5 weight percent.
- 10 14. A method as claimed in any one of the preceding claims wherein the gelling composition additionally comprises a buffering agent having a buffering capacity at a pH of up to about 5.5.
- 15 15. A method as claimed in Claim 14 wherein the buffering agent is present in the gelling composition at a concentration in the range 0.001 to 10% by weight based on the weight of the gelling composition.
16. A method as claimed in any one of claims 3 to 15 wherein the cross-linking agent is a polyvalent metal compound selected from the group consisting of polyvalent compounds of zirconium, titanium, aluminum, iron, chromium, hafnium, niobium and antimony.
- 20 17. A method as claimed in Claim 16 wherein the concentration of crosslinking agent in the gelling composition is from 0.001 to 0.5 weight percent based on the concentration of the polyvalent metal.
18. A method as claimed in any one of Claims 2 to 17 wherein the well is shut-in for a period of up to 50 hours before putting the well back on production.
- 25 19. A method as claimed in any one of the preceding claims wherein the amount of production chemical in the gelling composition is in the range from 1-25% by weight.
20. A method as claimed in any one of the preceding claims wherein the production chemical is released into the formation fluid through thermal and/or biodegradation of the gel under the conditions encountered in the formation.
- 30 21. A method as claimed in Claim 20 wherein the gel starts to thermally degrade at a temperature in the range 50 to 150°C.
22. A method as claimed in any one of Claims 1 to 19 wherein the gelling

composition contains an effective amount of a gel breaker so as to provide controlled breaking of the gel.

23. A method as claimed in Claim 22 wherein the gelling composition comprises from 0.1 to about 10 wt% of gel breaker.

5 24. A delayed release gelling composition comprising (i) an aqueous liquid, (ii) an oil field or gas field production chemical, and (iii) a gellable polymer wherein the composition has a gelation rate of longer than 1 hour.

25. A delayed release gelling composition as claimed in Claim 24 wherein the gellable polymer has crosslinkable groups, and the composition additionally
10 comprises (iv) a crosslinking agent.

26. A delayed release gelling composition as claimed in Claims 24 or 25 wherein the oil or gas field production chemical is selected from the group consisting of (i) scale inhibitors, (ii) corrosion inhibitors, (iii) hydrogen sulphide scavengers and (iv) hydrate inhibitors.

15 27. A delayed release gelling composition as claimed in any one of Claims 24 to 26 wherein the production chemical is suspended in the aqueous liquid in the form of particles having a particle size of 100% less than 10 microns.

28. A delayed release gelling composition as claimed in Claims 27 wherein the particles of production chemical are coated with a coating agent selected from water-
20 soluble polymers and oil-soluble polymers.

29. A delayed release gelling composition as claimed in any one of Claims 24 to 28 wherein the gellable polymer is selected from the group consisting of biopolysaccharides, cellulose ethers and acrylamide-containing polymers.

30. A delayed release gelling composition as claimed in any one of Claims 24 to 29
25 wherein the concentration of the gellable polymer in the gelling composition is in the range of about 0.01 to 0.5 weight percent.

31. A delayed release gelling composition as claimed in any one Claims 24 to 30 wherein the gelling composition additionally comprises a buffering agent having a buffering capacity at a pH of up to about 5.5.

30 32. A delayed release gelling composition as claimed in Claim 31 wherein the buffering agent is present in the gelling composition at a concentration in the range 0.001 to 10% by weight based on the weight of the gelling composition.

33. A delayed release gelling composition as claimed in any one of Claims 25 to 32

wherein the cross-linking agent is a polyvalent metal compound selected from the group consisting of polyvalent compounds of zirconium, titanium, aluminum, iron, chromium, hafnium, niobium and antimony.

- 5 34. A delayed release gelling composition as claimed in Claim 33 wherein the concentration of crosslinking agent in the gelling composition is from 0.001 to 0.5 weight percent based on the concentration of the polyvalent metal.
35. A delayed release gelling composition as claimed in any one of Claims 24 to 34 wherein the amount of production chemical in the gelling composition is in the range from 1-25% by weight.
- 10 36. A delayed release gelling composition as claimed in any one of Claims 24 to 35 wherein the gelling composition contains an effective amount of a gel breaker so as to provide controlled breaking of the gel.
37. A delayed release gelling composition as claimed in Claim 36 wherein the gelling composition comprises from 0.1 to about 10 wt% of gel breaker.
- 15 38. Use of a delayed release gelling composition as defined in any one of Claims 24 to 37 to treat a hydrocarbon-bearing porous subterranean formation by injecting the gelling composition into the porous subterranean formation and forming a gel within the pores of the formation thereby encapsulating the production chemical in the gel.